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DETERMINATION OF ORGANOTIN STRUCTURES IN ANTIFOULING COATINGS B--ETC(U)

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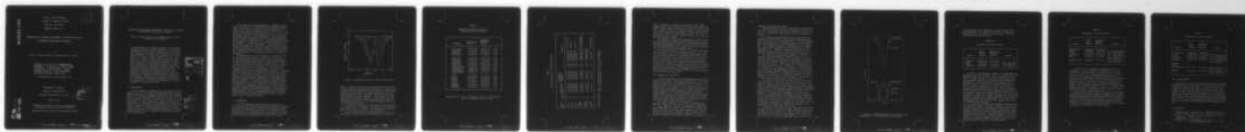
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DETERMINATION OF ORGANOTIN STRUCTURES IN ANTIFOULING COATINGS

BY MÖSSBAUER SPECTROSCOPIC TECHNIQUES

by

Elmer J. O'Brien, Charles P. Monaghan and Mary L. Good

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DETERMINATION OF ORGANOTIN STRUCTURES IN ANTIFOULING COATINGS  
BY MÖSSBAUER SPECTROSCOPIC TECHNIQUES

Elmer J. O'Brien, Charles P. Monaghan and Mary L. Good  
University of New Orleans

In characterizing the leaching properties of antifouling coatings containing organotin compounds, it has become necessary to determine the structure of the tin species in the coating. An extensive investigation of the Mössbauer parameters of numerous tin compounds of the type  $R_3SnX$  ( $R$  = n-butyl, n-propyl, phenyl;  $X$  = I, Br, Cl, OH, OAc, F) has shown that the quadrupole splitting parameter and  $\rho$  (ratio of isomer shift to quadrupole splitting) are related to the molecular geometry. The Mössbauer parameters for organotin polymers used in antifouling coatings and conventional coating formulations containing organotin compounds have been obtained. The quadrupole splitting and  $\rho$  value in these cases are sensitive to structural changes which occur in the organotin compounds upon incorporation into these coating matrixes. Mössbauer studies have been performed on the compounds  $[(C_4H_9)_3Sn]_2O$ ,  $(C_4H_9)_3SnOAc$ ,  $(C_4H_9)_3SnF$  in various matrices and solvent systems, and the results are discussed in the context of the behavior of these compounds in the coating systems.

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# I. INTRODUCTION

Certain organotin compounds of the type  $R_3SnX$  ( $R$  = alkyl, phenyl;  $X$  = Cl, F, OAc, etc.) have been employed in coating formulations as marine antifouling additives. The effectiveness of the coating is dependent upon the identity of the tin species, the concentration of the solvated tin species at the coating surface, and the leach rate of the tin species out of the coating. In many coatings the organotin compounds are added directly to the basic paint formulations, but recently polymers containing organotin pendant groups have been synthesized and tested for antifouling effectiveness. To fully characterize the role of the organotin components, the identity and structure of the tin species in the various coatings must be ascertained.

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The quadrupole splitting parameter in Mössbauer spectroscopy is sensitive to the geometry of the electronic field about the tin moiety, and the isomer shift parameter is indicative of the electron density at the tin nucleus which assists in assigning the oxidation state of the tin (1). Some researchers have also used the parameter  $\rho$ , the ratio of the quadrupole splitting to the isomer shift (relative to  $\text{SnO}_2$ ), as an empirical relationship indicative of the coordination number of tin(IV) compounds (2,3). A  $\rho$  value greater than 2.1 is considered to be indicative of a coordination greater than four; whereas, a  $\rho$  value less than 1.8 is considered to be indicative of four-fold coordination. This relationship is based on the observation that the isomer shift values generally decrease and that the quadrupole splitting values increase with coordination numbers greater than four. By examining  $\rho$  values the geometry of the organotin species in a coating can be deduced.

The Mössbauer data in the literature are characterized by discrepancies from author to author (4). Many of the earlier measurements were taken with crude instrumentation on compounds of questionable purity. Variations in data due to crude instrumentation are to be expected but the effect of a compound's purity is more subtle. Figure 1 shows a Mössbauer spectrum of impure  $[(\text{C}_4\text{H}_9)_3\text{Sn}]_2\text{O}$ . The spectrum was first interpreted as two lines giving an isomer shift of 1.25mm/sec and a quadrupole splitting of 1.64mm/snc. The compound was determined to be impure and the spectrum was eventually fit to four lines, indicating the presence of two compounds. After purifying  $[(\text{C}_4\text{H}_9)_3\text{Sn}]_2\text{O}$  by vacuum distillation and taking another Mössbauer spectrum, the new measurement yielded an isomer shift of 1.26mm/sec and a quadrupole splitting of 1.49mm/sec. To provide acceptable working standards for determining the chemical and physical parameters of tin moieties in the coatings of interest, it has been necessary to redetermine the Mössbauer parameters for a wide variety of carefully characterized organotin compounds. This report contains our initial studies on the applicability of Mössbauer spectroscopy as a tool in determining the chemical characteristics and solid state structures of the organotin species used in marine antifouling coatings.

## II. EXPERIMENTAL

The  $^{119}\text{Sn}$  Mössbauer data were obtained on an Austin Science Associates constant acceleration spectrometer operated in conjunction with a Nuclear Data 2200 multichannel analyzer. The source was  $\text{Ba}^{119}\text{SnO}_3$ , obtained from New England Nuclear Corporation, at an activity of 10 mCi. The data was collected with the source at room temperature and the absorber at 77°K. No correction has been made for the second order Doppler

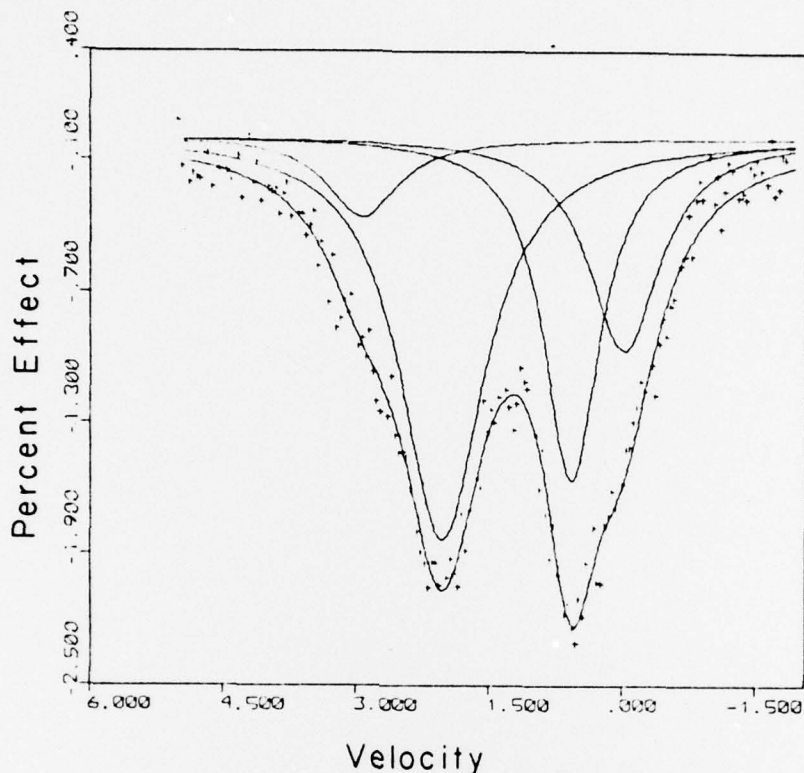


Figure 1. Mössbauer spectrum of impure  $[(C_4H_9)_3Sn]_2O$ .

effect. Velocity calibration was accomplished with an Austin Science Associates laser interferometry system. Spectra were corrected for the displacement of the source from equilibrium position and then fitted to a sum of Lorentzian curves by a least squares procedure. All isomer shift values are referenced to  $BaSnO_3$  at room temperature. The results for  $R_3SnX$  compounds are presented in Table I, and the results for organotin species in various coatings are presented in Table II. All reported parameters are the weighted averages obtained from at least two spectra.

The organotin compounds were acquired from M&T Chemicals, Inc. and were used as received. All organotin compounds have been analyzed for C, H, and Sn. The formulations presented in Table I are consistent with the results obtained.

Frozen solution samples were prepared by placing a 10% solution in a liquid cell and quick freezing in liquid nitro-

TABLE I  
Mössbauer Parameters for Various  
Organometallic Tin Compounds\*

Compound	Isomer Shift (mm/sec)	Quadrupole Splitting (mm/sec)	$\rho$
$(C_3H_7)_3SnCl$	$1.563 \pm 0.004$	$3.438 \pm 0.009$	2.228
$(C_3H_7)_3SnBr$	$1.51 \pm 0.02$	$3.24 \pm 0.04$	2.14
$(C_3H_7)_3SnI$	$1.57 \pm 0.01$	$2.89 \pm 0.02$	1.84
$[(C_3H_7)_3Sn]_2O$	$1.28 \pm 0.02$	$1.50 \pm 0.03$	1.17
$(C_4H_9)_3SnF$	$1.422 \pm 0.002$	$3.871 \pm 0.006$	2.722
$(C_4H_9)_3SnCl$	$1.58 \pm 0.01$	$3.49 \pm 0.01$	2.21
$(C_4H_9)_3SnBr$	$1.56 \pm 0.04$	$3.32 \pm 0.06$	2.13
$(C_4H_9)_3SnI$	$1.56 \pm 0.02$	$2.88 \pm 0.03$	1.85
$(C_4H_9)_3SnOAc$	$1.439 \pm 0.003$	$3.531 \pm 0.005$	2.454
$[(C_4H_9)_3Sn]_2CO_3$	$1.46 \pm 0.06$	$3.65 \pm 0.08$	2.50
$[(C_4H_9)_3Sn]_2O$	$1.256 \pm 0.003$	$1.490 \pm 0.008$	1.186
$(C_4H_9)_3SnOMacr$	$1.458 \pm 0.005$	$3.62 \pm 0.01$	2.48
$(C_4H_9)_3SnOAcr$	$1.44 \pm 0.01$	$3.61 \pm 0.02$	2.51
$Ph_3SnF$	$1.257 \pm 0.005$	$3.65 \pm 0.01$	2.90
$Ph_3SnCl$	$1.35 \pm 0.01$	$2.54 \pm 0.01$	1.88
$Ph_3SnBr$	$1.40 \pm 0.01$	$2.45 \pm 0.01$	1.75
$Ph_3SnI$	$1.45 \pm 0.01$	$2.24 \pm 0.01$	1.54
$Ph_3SnOAc$	$1.32 \pm 0.01$	$3.35 \pm 0.01$	2.54
$Ph_3SnOH$	$1.19 \pm 0.01$	$2.84 \pm 0.01$	2.49
$[Ph_3Sn]_2O$	$1.16 \pm 0.01$	$1.38 \pm 0.01$	1.19

\*Abbreviations: -OAc is  $-O(CO)CH_3$ , -OMacr is  $-O(CO)C(CH_3)CH_2$ ,  
-OAcr is  $-O(CO)CHCH_2$ , and Ph is  $C_6H_5$ .

TABLE II  
Mössbauer Results on Coating Systems\*

Coating Type	Code	Isomer Shift (mm/sec)	Quadrupole Splitting (mm/sec)	$\rho$	Remarks
OMP-1	C	1.37 +0.02	2.69 +0.02	1.96	Contains TBT, TPT; 29.4% Sn
	U	1.47 +0.03	2.82 +0.03	1.92	by weight.
OMP-2	C	1.35 +0.02	2.70 +0.02	2.00	Contains TBT; 24.8% Sn
	U	1.42 +0.01	2.84 +0.01	2.00	by weight.
OMP-4	C	1.38 +0.02	2.69 +0.02	1.95	Contains TBT; 30.0% Sn
	U	1.40 +0.02	2.92 +0.02	2.09	by weight.
Paint 1020A	C	1.41 +0.02	3.76 +0.02	2.67	$(C_4H_9)_3SnF$ , 18.1% by weight.
	U	1.424+0.004	3.761+0.008	2.64	$[(C_4H_9)_3Sn]_2O$ , 4.2% by weight.
Paint Glidden	C	1.47 +0.02	3.45 +0.02	2.35	$[(C_4H_9)_3Sn]_2O$
	U	1.447+0.007	3.35 +0.01	2.32	9.1% by weight.
Alum-A-Tox	U	1.41 +0.01	3.56 +0.02	2.52	$(C_4H_9)_3SnF$ , 7.1% by weight.

\*Abbreviations: OMP = organotin polymer, TBT = tri-n-butyltin,  
TPT = tri-n-propyltin, C = cured, U = uncured.

gen. A liquid cell consists of a 3mm thick, 38mm x 51mm aluminum plate with a 13mm hole in the middle for holding the sample. Mylar windows are glued onto the plate and the solution is placed into the cell through a slot. The frozen solution state is assumed to represent an average description of the solution state at any one instant of time. All liquid samples were quick frozen in liquid nitrogen; crystallization is likely for pure liquids.

The organotin polymers were donated by E. Fischer of the D. Taylor Naval Ship Research and Development Center. OMP-1 is poly(tri-n-butyltin methacrylate/tri-n-propyltin methacrylate/methylmethacrylate), OMP-2 is poly(tri-n-butyltin methacrylate/methylmethacrylate), and OMP-4 is the tri-n-butyltin ester of poly(methylvinylether/maleic acid).

The coating designated "Glidden" is a conventional vinyl coating which contains  $[(C_4H_9)_3Sn]_2O$  as toxicant. The 1020A coating contains vinyl resin,  $(C_4H_9)_3SnF$ , and  $[(C_4H_9)_3Sn]_2O$ ; it is the Mare Island Paint Laboratory Formula 1020A. The Alum-A-Tox coating is also a conventional vinyl coating which contains  $(C_4H_9)_3SnF$  as toxicant. Since the coating matrix was also part of the study, several coatings were prepared using any one of the above coatings but which did not contain any toxicant. Toxicant was added to the coating so that tin would be 3.5% by weight. Mössbauer measurements were made on cured and uncured coatings. The coatings were cured by depositing thick films on Plexiglas<sup>®</sup> and letting the samples air-dry for at least four weeks.

### III. RESULTS AND DISCUSSION

It has been suggested in the literature that at low temperatures the organotin halides and hydroxides have structures similar to  $(CH_3)_3SnF$ . This compound is polymeric with trigonal bipyramidal ligand geometry about the tin atom (5). In Table I one can see that most of the  $\rho$  values are above 2.1 in agreement with this suggestion. Even though  $Ph_3SnCl$  has been found to have a tetrahedral structure at room temperature, it is also expected to form polymeric coordination chains (pentacoordinate tin) at low temperatures in spite of its low  $\rho$  value (6). One can argue that as the R group becomes more bulky, steric hinderance will prevent association; the Mössbauer data indicate that association is always present but to a variable degree, depending on the R group.

The crystal structure of  $(CH_3)_3SnOAc$  indicates that polymeric chains exist and that the tin is pentacoordinate (7). The  $\rho$  values for  $Ph_3SnOAc$ ,  $(C_4H_9)_3SnOAc$ ,  $(C_4H_9)_3SnOAc$ , and  $(C_4H_9)_3SnOMacr$  in Table I would indicate that these compounds also exist in the same pentacoordinate form although one might have expected significant steric hinderance from the bulky phenyl and butyl groups. Apparently the steric factors are rendered insignificant because of the large Sn-Sn

distances in the polymeric chains.

Infrared studies have shown  $[(C_3H_7)_3Sn]_2O$ ,  $[(C_4H_9)_3Sn]O$ , and  $[(Ph)_3Sn]_2O$  to have four-fold coordination about each tin atom (8). The Mössbauer measurements support this assertion as can be seen from the low  $\rho$  values for these compounds in Table I.

In interpreting the Mössbauer data on the coatings of interest, it must be kept in mind that the measurements are made at 77°K and not at room temperature. Although structures can be postulated for an organotin species at a low temperature, the extrapolation to room temperature may not be possible. As an example,  $Ph_3SnCl$  is tetrahedral at room temperature but has been postulated to be pentacoordinate at low temperatures (6). Mössbauer techniques should be limited to identifying components and to specifying structures only under the conditions where no phase transitions are expected.

Upon comparing the Mössbauer parameters of the tin species in the organometallic polymers in Table II to the organotin compounds in Table I, it is noted that none of the  $(C_3H_7)_3SnX$  or  $(C_4H_9)_3SnX$  compounds have Mössbauer parameters similar to those of the  $(C_4H_9)_3Sn-$  or  $(C_3H_7)_3Sn-$  moieties in the organotin polymers. The  $\rho$  values are inconclusive as to the coordination of the tin. A reduction in the magnitude of the  $\rho$  values for the organometallic polymers versus the pure  $(C_4H_9)_3SnOAc$  and  $(C_4H_9)_3SnOMac$  compounds is to be expected since the pendant organotin groups are postulated to be far apart in the polymers. The coordination about the tin atom is expected to be four and the  $\rho$  value is expected to be low. A reduction in the  $\rho$  value is seen; however, it is higher than one would expect for simple four-fold coordination.

The results of measurements on the commercial 1020A coating match those of  $(C_4H_9)_3SnF$ , indicating no change in this organotin compound upon incorporation into the coating. The peaks for  $[(C_4H_9)_3Sn]_2O$  are not observed in the 1020A coating. As shown below the  $[(C_4H_9)_3Sn]_2O$  may be chemically transformed into a species having Mössbauer parameters similar to those of  $(C_4H_9)_3SnF$  thus obscuring the presence of this starting material. The spectrum of the commercial Glidden coating which contains approximately 10%  $[(C_4H_9)_3Sn]_2O$  is interesting in that the parameters are significantly different from the parent compound (see Figure 2), indicating extensive chemical modification of the organotin species in the coating. Since the Mössbauer parameters of  $(C_4H_9)_3SnF$  are similar to those of  $(C_4H_9)_3SnF$  in the Alum-A-Tox coating, the compound is not altered when it is mixed into the coating.

The Mössbauer parameters for pure  $(C_4H_9)_3SnF$  and for this compound mixed into the 1020A, Glidden, and Alum-A-Tox vinyl coatings are given in Table III. Both the isomer shifts and the quadrupole splittings of  $(C_4H_9)_3SnF$  in the coatings are very similar to those of the pure compound. This result suggests that small crystals of  $(C_4H_9)_3SnF$  remain intact in all

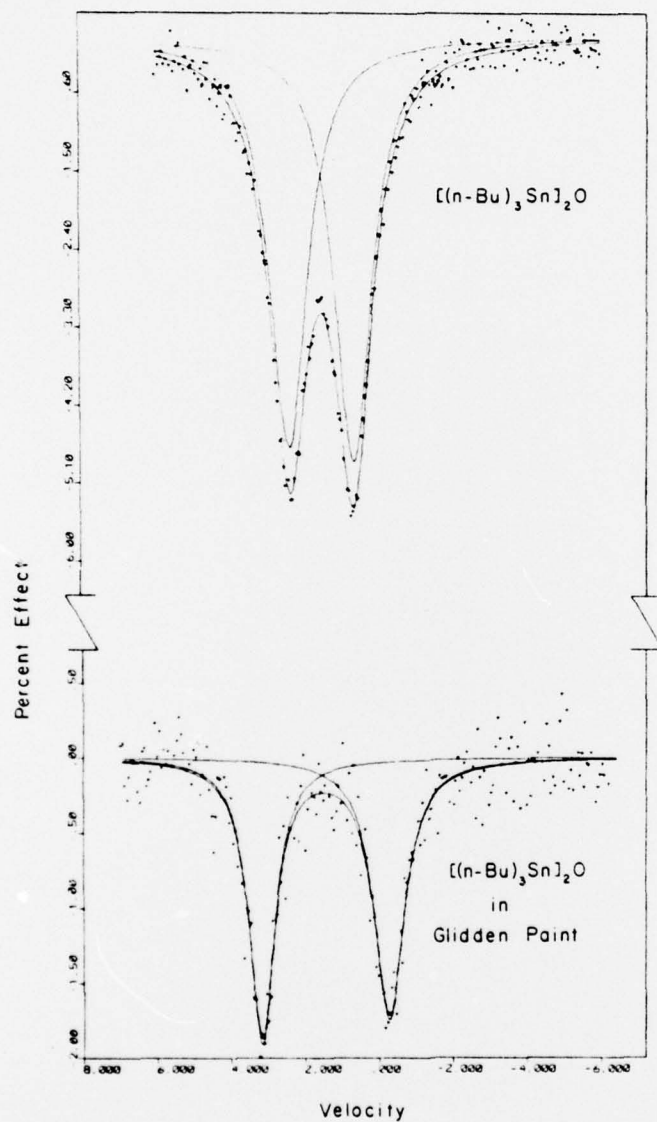


Figure 2. Mössbauer spectra of  $[(C_4H_9)_3Sn]_2O$  and  $[(C_4H_9)_3Sn]_2O$  in the commercial Glidden coating.

of the matrices. When  $(C_4H_9)_3SnF$  is mixed into the 1020A coating containing no pigment or toxicant, a suspension is formed which does not appear to be homogeneous. The suspended material rapidly settles.

TABLE III

 $(C_4H_9)_3SnF$  in Various Matrices

Matrix	Isomer Shift (mm/sec)	Quadrupole Splitting (mm/sec)	Remarks
$(C_4H_9)_3SnF$	1.422+0.002	3.871+0.006	
1020A	1.417+0.005	3.77 +0.01	9.4% $(C_4H_9)_3SnF$
Glidden	1.416+0.009	3.72 +0.02	9.4% $(C_4H_9)_3SnF$
Alum-A-Tox	1.42 +0.02	3.68 +0.03	9.4% $(C_4H_9)_3SnF$

In Table IV the Mössbauer parameters for  $(C_4H_9)_3SnOAc$  in various matrices are presented. All of the isomer shifts and quadrupole splittings are very similar, regardless of the matrix. Okanara and Ohara (9,10) have shown that triethyl- and tripropyltin formates are associated when dissolved in cyclohexane. Simons and Graham have also shown that trimethyltin formate is associated in methylene dibromide but that the acetate is monomeric in dilute solutions (11). Since the matrix apparently has no affect on the Mössbauer parameters, one can conclude that  $(C_4H_9)_3SnOAc$  is associated in the solid state, in the frozen solutions studied, and in the coatings. Upon mixing  $(C_4H_9)_3SnOAc$  into the 1020A coating containing no pigment or toxicant, a translucent solution is obtained. The toxicant is widely dispersed in the matrix and the mixture appears to be homogeneous. In the solid state  $(C_4H_9)_3SnOAc$  would therefore be a high polymer and in solutions it would a low polymer.

As can be seen from Table V the quadrupole splitting of the organotin species in the 1020A, Glidden, or in the Alum-A-Tox coating to which  $[(C_4H_9)_3Sn]_2O$  has been added does not match the quadrupole splitting of pure  $[(C_4H_9)_3Sn]_2O$ . This suggests a structural change of  $[(C_4H_9)_3Sn]_2O$  upon incorporation into these coatings. Considering the magnitude of the quadrupole splitting of the organotin species in the 1020A coating, it is not surprising that the presence of this compound in the commercial 1020A coating was obscured by the  $(C_4H_9)_3SnF$  which is present in greater quantity.

TABLE IV  
 $(C_4H_9)_3SnOAc$  in Various Matrices

Matrix	Isomer Shift (mm/sec)	Quadrupole Splitting (mm/sec)	Remarks
$(C_4H_9)_3SnOAc$	$1.439 \pm 0.003$	$3.531 \pm 0.006$	
1020A	$1.439 \pm 0.006$	$3.54 \pm 0.01$	10.6% $(C_4H_9)_3SnOAc$
Glidden	$1.44 \pm 0.01$	$3.49 \pm 0.02$	10.6% $(C_4H_9)_3SnOAc$
Alum-A-Tox	$1.453 \pm 0.008$	$3.55 \pm 0.02$	10.6% $(C_4H_9)_3SnOAc$
$CHCl_3$	$1.45 \pm 0.01$	$3.63 \pm 0.03$	10% $(C_4H_9)_3SnOAc$ Frozen Solution
n-butylacetate	$1.464 \pm 0.007$	$3.54 \pm 0.01$	9.97% $(C_4H_9)_3SnOAc$ Frozen Solution

A comparison of the Mössbauer parameters of pure  $[(C_4H_9)_3Sn]_2O$  to this compound in various frozen solutions (see Table V) indicates that a considerable solvent interaction is present. The  $[(C_4H_9)_3Sn]_2O$  species in the Alum-A-Tox coating is probably the same solvated species as is present in the xylene-methyl isobutyl ketone solution which is the solvent for that coating, but it is not the same as the organotin species in the other coatings or frozen solutions. Infrared studies indicate that an organotin carboxylate is formed in the 1020A and Glidden coatings (12). The Mössbauer studies have neither confirmed nor refuted this finding. The unusual behavior of  $[(C_4H_9)_3Sn]_2O$  in these coatings and solvents is the object of current research.

These initial results indicate the potential of Mössbauer spectroscopy for identifying organotin components of various marine antifouling coatings and for determining the structure of the organotin species in these matrices. Further delineation of the coatings and model chemical systems is presently underway as is an evaluation of the Mössbauer backscatter technique for determining the organotin species on the surface as opposed to those found in the bulk samples.

TABLE V  
 $[(C_4H_9)_3Sn]_2O$  in Various Matrices

Matrix	Isomer Shift (mm/sec)	Quadrupole Splitting (mm/sec)	Remarks
$[(C_4H_9)_3Sn]_2O$	1.256+0.003	1.490+0.008	
1020A	1.439+0.007	3.38 +0.01	10.8% $[(C_4H_9)_3Sn]_2O$
Glidden	1.462+0.007	3.28 +0.01	11.2% $[(C_4H_9)_3Sn]_2O$
Alum-A-Tox	1.362+0.006	3.06 +0.01	11.0% $[(C_4H_9)_3Sn]_2O$
m-xylene	1.39 +0.02	2.67 +0.04	9.3% $[(C_4H_9)_3Sn]_2O$ Frozen Solution
Xylenes			
Methyl-			
isobutylketone	1.29 +0.01	2.91 +0.03	10.9% $[(C_4H_9)_3Sn]_2O$ Frozen Solution
Benzene	1.32 +0.01	2.55 +0.02	10.2% $[(C_4H_9)_3Sn]_2O$ Frozen Solution

#### IV. ACKNOWLEDGEMENT

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rho  
polymers used in antifouling coatings and conventional coating formulations containing organotin compounds have been obtained. The quadrupole splitting and  $\rho$  value in these cases are sensitive to structural changes which occur in the organotin compounds upon incorporation into these coating matrixes. Mössbauer studies have been performed on the compounds  $[(C_4H_9)_3Sn]_2O$ ,  $(C_4H_9)_3SnOAc$ ,  $(C_4H_9)_3SnF$  in various matrices and solvent systems, and the results are discussed in the context on the behavior of these compounds in the coating systems.